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Chitosan-Graphene Oxide Nanocomposites: A Potential Candidate for Waste Water Treatment

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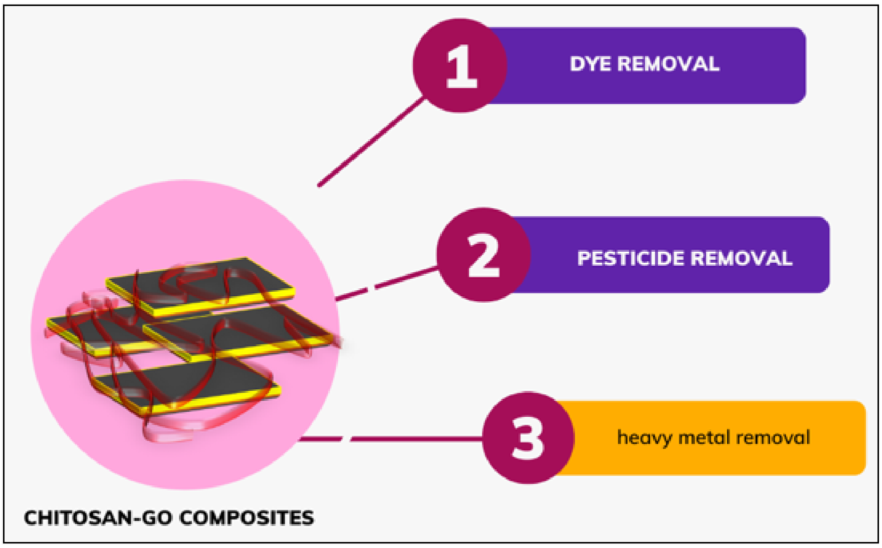
Abstract: ***Chitosan composites are considered to be one of the most efficient group of materials in water purification procedures. Chitosan is widely available natural polymer which could be processed easily into films, hydrogels, and aerogels. The nanocomposites of chitosan with various nanofillers also finds huge applications in water treatment. Amongst the nanofillers, the 2-D nanofillers such as graphene, graphene oxide, reduced graphene oxide, magnetic nanoparticle decorated graphene oxide shows exceptional performance owing to its unique physical and chemical characteristics. The current review covers these aspects in detail.***

Keywords: Chitosan, Graphene Oxide, Water treatment, Dye removal



1. Introduction

The ever-increasing world population demands multiple amenities, and when trying to meet all these demands on one end we are sacrificing on the other end. The rapid industrial growth across the globe has helped people across nations to improve the quality of life in a less expensive manner. But along with the pros, the cons also have to be addressed. One of the major repercussions of the ongoing upsurge in the population and the industrial growth is the less availability of clean water. According to the UN reports, around 2.1 billion people across the globe still lacks safely managed drinking water.

Collection and reuse of wastewater from the industries as well as from the households are the best method to face this challenge of water scarcity. But proper water treatment becomes necessary for the safer reuse, and it is a major responsibility of the scientific community to look after suitable materials and methods by which the waste water could be converted to a reusable form. Industrial waste water generally contains dyes, pigments, heavy metals, drugs, oils etc. The conventional methods for water purification includes screening, filtration, and sedimentation.[1] But these techniques are considered to be time consuming and less effective. Methods like reverse osmosis, forward osmosis, filtration, microfiltration, ion exchange techniques, and electrolysis (Fig. 1). are far more superior in terms of efficiency of water purification.[1] But these systems need more operational and initial investment cost.[2] Apart from these, photocatalysis, membrane filtration, and deactivation of pathogenic microorganisms have also gained interest in the research community.[3,4]

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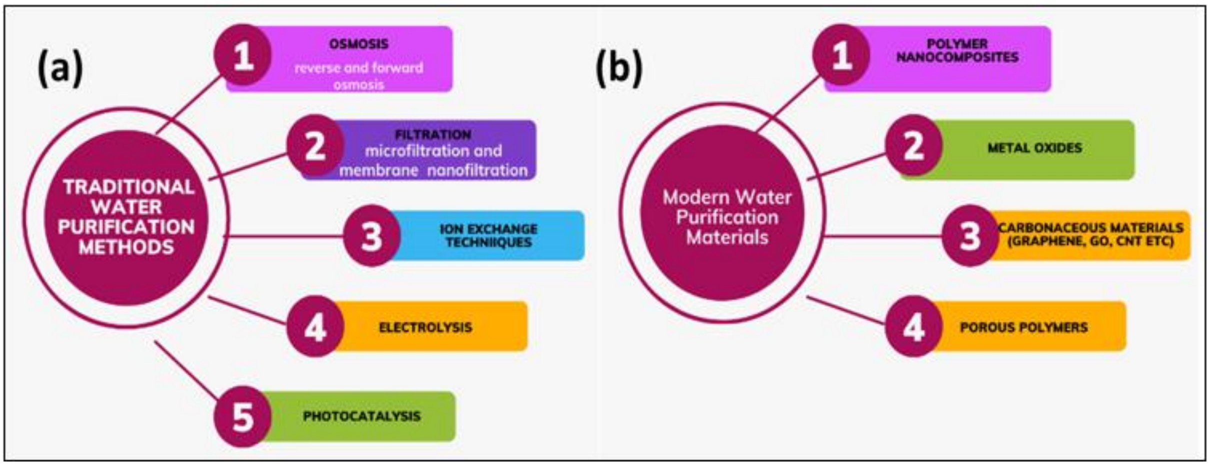

Figure 1: (a) Some of the traditional methods and (b) modern materials used for water purification

Recently, a number of nanomaterials because of their unique characteristics such as high surface area and improved physical and chemical properties, have been utilised for the water purification process mainly by adsorption and filtration methods. For example, carbonaceous nanomaterials such as carbon nanotubes, functionalised carbon nanotubes, carbon nanofibers, graphene, graphene oxide etc. are widely employed as good sorbents for the removal of aromatic hydrocarbons, dyes, and heavy metals .[5,6,7,8,9] Metal oxide nanomaterials such as titania, iron oxide, nano alumina etc. are also frequently used adsorbents for the removal of various pollutants.[10] Natural and synthetic polymers in its various forms like porous polymers, nano polymers, polymeric composites, and co-polymers. are also very competent candidates for the purification of waste water.[11]

In the current review we focus on the applications of chitosan and graphene oxide hybrid for the water purification purpose. Chitosan is a widely available biodegradable and biocompatible co-polymer of D-glucosamine and N-acetyl D-glucosamine.[12] It is generally prepared by the deacetylation of chitin, which is the second most abundant biopolymer after cellulose. Sources of chitin in nature includes shells of crab, shrimp, cell walls of yeast, fungi etc.[13] Structurally chitin and chitosan are quite similar to the cellulose, all of these are naturally occurring polysaccharides and the backbone remains the same in all. The hydroxyl group at C-2 position in cellulose is replaced by acetamide group in chitin, whereas in chitosan, this acetamide group is deacetylated resulting in an amino group at the C-2 position (see the Fig. 2).[14] In the copolymer, if the amount of glucosamine unit is above 50 % it is considered to be chitosan. The percentage of deacetylation is directly related to the amount of glucosamine content, and can vary from 50% to 100 % and can affect the properties such as the solubility, mechanical stability, and crystallinity. Chitosan is generally insoluble in water and organic solvents. However, it becomes easily soluble in aqueous solution whose pH is less than five and will exist as a cationic polysaccharide[15]. This biodegradable and biocompatible natural polymer is identified to be a well-suited replacement for the synthetic polymers due to its less toxicity, thermal and mechanical stability. Because of its versatile properties, it is widely used in medical and pharmaceutical filed, agricultural field, water purification etc.[16]

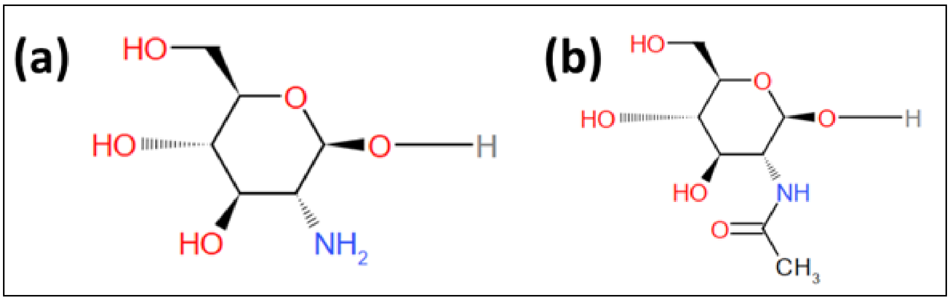

Figure 2: Structure of (a) chitosan, (b)chitin

Graphene oxide (GO) is considered to be the next generation sorbent to remove potential pollutants such as pesticides, dyes, drugs, and heavy metals from water.[17,18,19] This extremely high sorption behaviour of graphene oxide is owing to its peculiar structure. GO is having a two-dimensional arrangement of sp^2 hybridised carbons with a honey comb structure. Unlike graphene, which is unfunctionalized, in GO there are many oxygenated functional groups like hydroxyl groups, carboxyl groups, epoxy groups etc. This functional group improves the water solubility of GO and thus GO is highly water soluble in nature whereas the parent material graphene is completely hydrophobic and insoluble in water. Along with the improved water solubility, the functional groups on the periphery of the 2D carbon nanosheets also plays an important role in binding with various pollutants such as anionic and cationic dyes, various drugs etc. [20] Electrostatic interactions, hydrogen bonding, Vander Waals attraction etc. are possible between GO and various kinds of pollutants causing the effective adsorption of these on to GO and thereby increasing the efficiency of extraction. Fig. 3 shows the schematic representation of types interaction between GO and various organic pollutants.

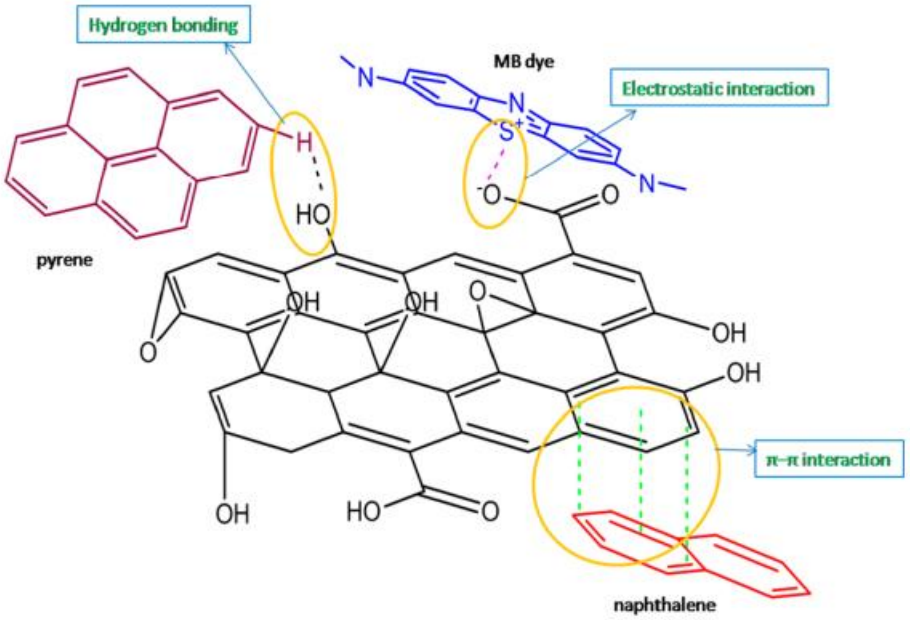

Figure 3: Schematic representation of types interaction between GO and various organic pollutants (printed with permission from *J. Chem. Eng. data* **2019**, *64* (3). Copyright {2019} American Chemical Society.[21]

Although graphene oxide is a very effective sorbent, sometimes when the use of it intended for excess amount of pollutants where more amount of GO becomes necessary, the problem of agglomeration of the nanosheets arises, which decreases its effectiveness.[22] The addition of surfactants may prevent the coagulation of GO sheets, but it will lead to the reduction in its sorption efficiency[23]. Recently, the polymer composites of GO have gained widespread attention due to the fact that a small percentage of Go in the polymer matrix can act as a multifunctional filler to improve the properties of the polymer such as its thermal, electrical and mechanical strength, antimicrobial and antibacterial activity etc along with increased adsorption of pollutants[24].Polymer processing techniques such as melt mixing, solution blending, in-situ polymerization etc. has been utilised to prepare a number of composites of various engineering polymers, conducting polymers, and insulating polymers. For example, Xu. Et.al synthesised a mechanically stable and flexible composite of PVA-GO (polyvinyl alcohol) by a solution bending process. They have utilised water as the solvent for solution blending, since PVA is a well-known water-soluble polymer and GO is also easily dispersible in water due to the presence of extensive functional groups. The vacuum filtration employed after the blending has resulted in an ordered layered arrangement of the GO sheets in the PVA matrix.[25] Polymers that could not be dissolved in water, but are soluble only in organic solvents could also be reinforced with GO by suitably adjusting various parameters such as solvent type, surfactant etc. For example PMMA-GO composites are widely used for medical applications, and dye removal.[26] Another one major engineering polymer is PVC due to its low cost, easy processing, and chemical stability s. The GO composites of PVC synthesised is also studied for different applications. For instance, Khan et.al studied the heavy metal removal capacity of the Graphene oxide/PVC composite papers functionalized with *p*-Phenylenediamine. They have observed that a variety of metals could be removed from the aquatic sample by the electrostatic interaction between the metal ions and the composite paper. In addition the composite papers could be easily recyclable and the same paper could be utilised for several cycles.[27] Another interesting application of PVC GO composites were reported by Hossain et.al, in which the composites prepared were intended for the use as the sole of the footwears. This composite sole showed better thermal and mechanical stability along with less more durability and lightweight.[28] Insoluble polymers such as epoxies find huge applications in materials science and the composites of this with GO is also equally important because of its ecstatic properties. However, solution blending or melt mixing cannot be employed for these categories of polymers. Therefore, a direct mixing of GO in clear epoxy resin followed by curing with the help of suitable curing agents could be utilised to prepare the composites. For example, An et.al studied the structure and properties of Silicon dioxide modified GO-epoxy composites and observed that the composites possess high tensile strength, high energy storage modulus, increased dielectric constant and decreased dielectric loss in comparison with the pristine epoxy polymer.[29]

Since chitosan can form some amido linkage with the carboxyl group of GO, the composites formed are found to be highly dispersible without any kind of agglomeration. This interaction is possible, when the GO is dispersed in water, because the carboxyl and hydroxyl groups on the surface of GO gain a negative charge due to the ionization. At the same time, -NH_2 group of chitosan attains a positive charge due to protonation and the polymer will exist as a cationic polysaccharide. When combined together these two will interact effectively and will result in a well dispersed composite.[30] The addition of chitosan, an already known adsorbing material, when combined with GO can prevent the coagulation and can increase the adsorption of various pollutants due to the synergic effect of both the materials. In the current review, we focus on the applications of GO-chitosan hybrid materials for the water treatment purpose for the removal of a number of pollutants.

2. Synthesis Methods

The chitosan GO composite can exist as simple dried composite, as hydrogels or as aerogels depending on the synthesis conditions. Geneal synthesis procedure involves dispersing the GO in distilled water, tapping the advantage of its highly hydrophilic nature and then mixing it homogeneously with the chitosan solution dissolved in dilute acetic acid solution (Fig. 4).[31] To improve the overall properties of the composites, many researchers have prepared the hybrids of GO with other nanoparticles and incorporated the same to chitosan through the same synthesis procedure for simple chitosan GO composites. For example, Zhang et.al synthesised the magnetite GO by the coprecipitation of salts on to GO sheets and thereafter fabricated the composites by solution blending method followed by magnetic separation and freeze drying.[32]

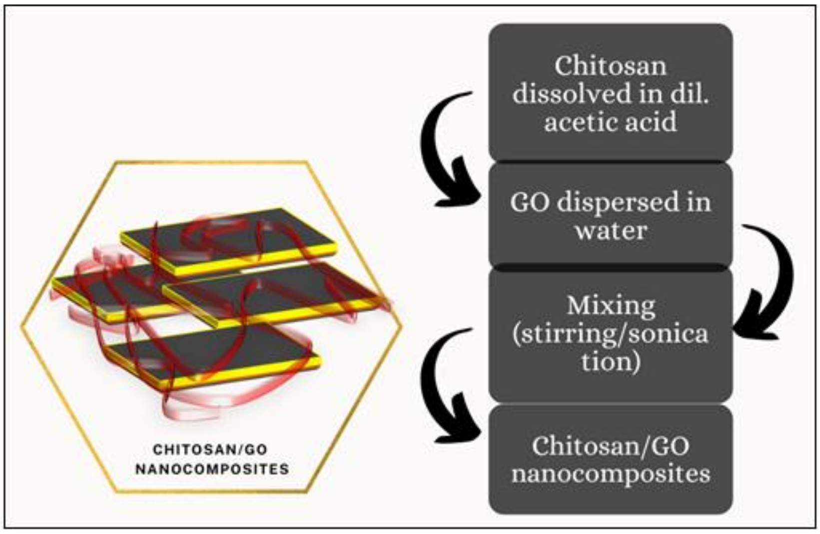

Figure 4: Schematic diagram and synthesis procedure for chitosan-GO composites

3. Applications of CS-GO

Since chitosan is a natural polymer with exceptional biological properties like biodegradation capacity, biocompatibility, high oxygen permeability, antimicrobial activity, and film forming capacity. it is widely used in the biomedical field, food packing, water purification etc. The composites of chitosan with GO enhance the properties of each component synergistically, as in GO helps to enhance the thermal and mechanical stability of the polymer and the polymer takes care of the biocompatibility factor of GO. For example, chitosan composites with GO are widely used as an efficient and smart food packaging material. Ahmed et.al showed that the packaging film made up of GO-chitosan exhibited much better tensile and mechanical strength along with antimicrobial and enhanced barrier properties.[33] The natural scaffolds, like the biopolymer chitosan also finds immense interest for the bone replacement since it can easily mimic the natural bone. However the polymeric scaffolds may sometimes lack the necessary mechanical and thermal stability.[34] These properties could be easily tailored with the addition of nanomaterials, especially the 2D materials like graphene and GO. For example, Kolanthai et.al synthesised a porous scaffold of a biopolymer system containing Alginate-Chitosan-Collagen incorporated with GO. The studies have shown that GO helps to maintain the mechanical stability and can help to form a free standing biocompatible porous structure which is also stable in biological medium and thus could be used as a replacement material in tissue regeneration[35]. Another important biomedical application of chitosan GO composites is in the wound healing process. Skin is one of the important and prominent organ of our body and wound healing in case of any injury is very important as it helps in the recovery, prevention of infection through the wound etc.[36] Wang et.al showed that the bio-nanocomposites of CS-functionalized GO shows sufficient enough mechanical stability and the wound healing studies conducted on the rat showed wound closure rate reached up to 92.2% after 21 days. [37] Cancer treatments and other diseases treatment using the controlled drug delivery systems based on the CS-GO composites are also one of the wide studied application of these composites. [38] Studies conducted by Kumar et.al shows that the chitosan -GO composites beads could be used as an effective controlled drug delivery of oral drug Metronidazole, used for the antibacterial and amoebic infection. [39] The use of GO-chitosan composites is not limited to any one field. This material is even found to be suitable as flexible substrates in supercapacitors for energy storage purpose. The composite of chitosan GO activated with VO_2 is found to have a very good energy density suitable for practical applications. The chitosan helps to prevent the stacking of GO sheets and also helps in the uniform distribution of the active VO_2 by bonding with the N atom of chitosan[40]. Fig. 5 summarizes some of the important applications of chitosan-GO composites.

Even though the technologies are well developed for water treatment, still the shortage of pure water is a concerning issue and new methods and materials become very much essential to overcome this issue. The current review focuses the applications of chitosan GO and chitosan modified GO for water purification purpose. The upcoming sections discusses certain important areas of water purification where chitosan-GO found in-depth applications.

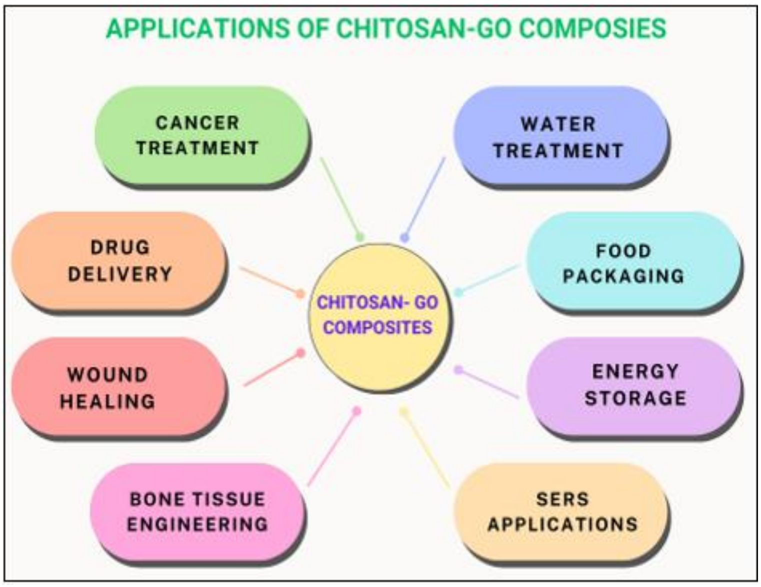

Figure 5: Some important applications of chitosan-GO composites

4. Removal of Heavy Metals

The presence of various heavy metals discharged into the water from various industrial sources is one of threatening problems which increases the scarcity of drinking water. Among the heavy metals, the non-biodegradable and highly toxic Cr(VI) and Cu(II), Pb (II) etc. are of detrimental effect and mostly carcinogenic and cause many other chronic disorders even at low concentration.[41] Toxic metals are generally originated naturally as well as by human intervention. Mining, transportation, electronic wastes, processing of the ores etc. are some ways by which the human pollute the water resources.[42],[43] Cr(VI) is considered to be a carcinogenic element and also cause skin damage if it gets adsorbed to the body.[44] Copper, which is widely used in coatings, plating, mining, brass manufacture etc. is also a prominent toxic heavy metal often seen in drinking water. As per the World Health Organizations protocols, the maximum acceptable concentration of Cu(II) in drinking water is 2.0 mg/L. Although many adsorbents such as carbon nanotubes, activated carbon, layered double hydroxide etc. are available to remove the heavy metals from water, a biodegradable adsorbent which is derived from biomass is more environmentally friendly and becomes more economically viable.[45], [46]Anush et. al showed that, the Schiff base formed from chitosan at the NH2 group at C2 position, when grafted with GO has a very good adsorption capacity towards Cu (II). The higher adsorption capacity of the Schiff base- GO composite formed from chitosan than the pristine chitosan is attributed to the higher number of nitrogen, sulphur and oxygen groups as well as the presence of carboxyl and hydroxyl groups on the surface of GO. They observed that, the adsorption is favoured at neutral pH, possibly due to the coordinate bond formation between the nitrogen and OH groups on the composite with the metal ions. The adsorption found to decreases at acidic pH, due to the possible protonation of the carboxylic groups and nitrogen atoms [47].

Lead is one of the most threatening heavy metal which is highly toxic not only for the human beings but also for the whole universe. Removal of lead from the water, which is mainly discharged from electrical industries, anti-fouling paints etc. are an important aspect of water purification. Natural biopolymers are an important category of adsorbent used for the removal of these lethal heavy metals. For example, Sharma et.al, have synthesised a cross-linked chitosan GO-chitosan by a two-step method including the sol gel technique followed by chemical cross linking and tested their capacity for the removal of one of the most toxic heavy metals, namely lead. The adsorption capacity at pH 5 was observed to be 566.5 mg/g , quite higher than other common adsorbents. Here, the chemical grafting increased the concentration of surface nitrogen groups, which in turn increased the adsorption capacity. The synthesised composites were also tested for desorption and that emphasised the reusability of the material. [48] The GO-chitosan aerogels are also a very important and widely used candidates for the removal of toic heavy metals. Different mechanisms such as electrostatic interactions from the functional groups of GO, chelation with the amino groups of chitosan, compleation and coordination with various functional groups etc. facilitates the adsorption of different metals such as Pb(II), Cu(II), Cr(IV) etc.

Even though chitosan is a very efficient adsorbent for heavy metals, its efficiency is found to be increased by the slight change in their surface chemistry by adding magnetic nanoparticles. L. Fan et.al synthesised a magnetic chitosan/graphene oxide composite where Fe_3O_4 has been used as the magnetic additive and is used for the removal of Pb(II) ions and found the maximum adsorption at pH 5. At low pH the adsorption was not so effective possibly due to the electrostatic repulsion. The composite showed 76.94 mg/g adsorption with the striking property of 90.03 % desorption, making the synthesised material a low cost, reusable adsorbent.[49] Table 1 summarizes the applications of chitosan-GO composites for the removal of heavy metals from water.

Table 1: Examples of chitosan-GO composites for heavy metal removal

Adsorbent used	Metal removed	% of the metal removed/ Adsorption capacity	Reference
CS/MGO chitosan/magnetite-graphene oxide composites	Cr(VI)	86.74%	32
fGOSB (Schiff base)	Cu (II)	111.11 mg/g	
cross linked chitosan GO-chitosan	Pb (II)	566.6 mg/g	48
Graphene oxide/chitosan aerogel microspheres	Pb (II)	747.5 mg/g	44
magnetic chitosan/graphene oxide	Pb (II)	76.94 mg/g	49

5. Treatment of dyes contaminated water

One of the major water pollutants across the globe is the synthetic dyes mainly discarded from the textile industries. Many of these synthetic organic dyes are highly toxic, not biodegradable and affect the water system and environment in a very detrimental way. and Most of the time, the wastewater from the textile industries is not treated properly before it is being rejected off to other water sources and this is estimated to cause 20 percentage of the total water pollution in the globe[50]. The accumulation of these dyes in water are hazardous to the existence of land and aquatic animals both, and is reported to be carcinogenic beyond certain levels. Therefore, the complete removal of the dyes is mandatory if the waste water from the textile industry is to be reused. Traditional methods such as sedimentation, filtration etc. and cannot completely remove the colour of the dyes, especially the anionic dyes from the water[46,51].

Chitosan, which is the only cationic polysaccharide biopolymer, with an -NH$_2$ group[52] is reported to be an efficient adsorbent for the removal of various anionic dyes such as Methylene blue[53] Acid orange 7 (AO 7), Methyl orange (MO)[54], remazol brilliant violet and procion yellow MX 8G dyes[55]. However, the adsorption of both the cationic and anionic dyes together using chitosan is not possible. Graphene oxide on the other hand, because of the extensive functionalisation is a good adsorbent for all types of dyes, but their colloidal stability is a huge drawback. If the chitosan is combined with GO by any means, it can reduce the coagulation and can increase the adsorption of the dyes. Along with the enhanced adsorption in the case of chitosan graphene oxide hybrids, it also possessed enhanced thermal and mechanical stability[51]. Many a times, the GO-chitosan hybrid will exist as hydrogels, since chitosan itself will act as a cross linking agent owing to the increased electrostatic interactions between both. The increase in viscosity caused by GO will also promote the hydrogel formation[56].

The adsorption of the organic dyes on to CS-GO, which is a surface phenomenon, could be either due to physisorption or due to chemisorption until the organic dye reaches a maximum adsorption or till it reaches a saturation state. Different kinetic models are used to explain the adsorption which includes Langmuir adsorption isotherm, Freundlich adsorption isotherm, BET etc[57].

For example, H. Mittal et.al, showed that the nanocomposite hydrogels of vinyl functionalised GO and chitosan acted as good adsorbents for cationic dyes such as methylene blue as well as for anionic dyes such as methyl orange[52]. In this study, they were able to achieve 99 % dye absorption for methylene blue at specified concentration and about 82 % dye absorption for methyl orange. The most widely adopted and the easiest technique for the adsorption studies are the column techniques, where the adsorbent is packed in the column and the waste water containing the dyes are passed and filtered through it. The filtration could be done either immediately after the passage or after immersing the packed column in the dye solution for a certain period of time. The time of interaction as well as the composition of the adsorbent with the dye solution will affect the efficiency of adsorption. Vo et.al, adopted this adsorption filtration method as shown in Fig. 6, for four dyes and observed that increased GO concentration will facilitate the adsorption of cationic dyes.

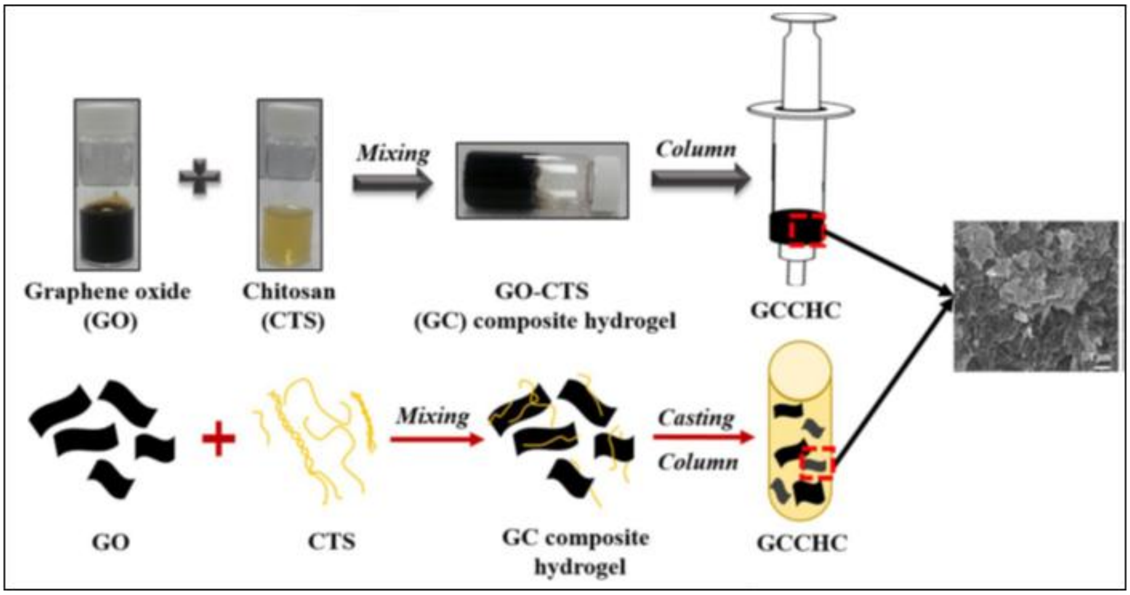

Figure 6: The schematic diagram showing the formation of chitosan-GO hydrogel and the column purification method adopted [51]

Along with the hydrogels, aerogels with very high porosity and thus extremely large surface area are also an important category of adsorbent used for the water purification. For example, graphene oxide/chitosan aerogel microspheres (GCAMs) with honeycomb-cobweb have been utilised for the removal of various cationic and anionic organic dyes and it is observed that, more than 80 % of adsorption happened within five minutes. The adsorption followed a Langmuir isotherm, where a uni-layer adsorption happened on the active sites[44].

Sabzevari et.al used the chitosan-GO composite for the removal of a model dye effluent, namely methylene blue and showed that the composite is having a greater adsorption capacity for methylene blue, and the kinetics follows a pseudo-second order trend. The increase in adsorption is assumed to be due to various factors such as alteration of the functional groups on the surface of the composite, cooperative interaction of the dye and composite etc. [20]

Abolhassani et.al has synthesized a chitosan graphene oxide membrane and utilised the same for the filtration of water containing dyes such as methylene blue and methyl orange. The membranes, even if they were of different morphology, structural order and chemical composition of GO and CS, all showed similar performance. Methylene blue has been removed upto 95 %, even for a concentration of 100mg/ml. For the methyl orange, the rejection observed for microscale grafted GO -chitosan was observed to be in the range of 68-99 % indicating sorption as the dominant mechanism of removal[58].

Incorporation of magnetic nanoparticles into GO has gained widespread attention for the adsorption purpose, owing to their unique properties such as high adsorption capability, separable nature from the liquid state, ability to reduce the aggregation of GO sheets etc. In a study conducted by Rebekah et.al, magnetic graphene oxide-chitosan nanocomposite, where the GO is decorated with Fe_2O_3 is utilised for the removal of 2-naphthol, a precursor of the organic dyes. Here, various parameters affecting the adsorption capacity, such as effect of adsorbent quantity, effect of initial concentration of adsorbate, pH, effect of contact time etc. were studied in detail. It was observed that, the adsorption tends to increase up to a level of adsorbent concentration, and beyond the optimum concentration, the adsorption capacity remained the same. Also, it has been observed that, maximum adsorption happened at the initial phase itself, owing to the availability of more surface sites. pH is a very important parameter in determining the adsorption capacity. In the present study, the authors observed a better adsorption at acidic pH. This is because the adsorbent possesses positive charge and the adsorbate become anionic and thus create an electrostatic interaction between them leading to better adsorption[59].

PVA incorporated chitosan hydrogels are also found to be some promising candidates for the adsorption dyes. Das et.al utilised Graphene oxide impregnated chitosan–PVA hydrogel nano polymer for the adsorption of the Congo red dye. Here also, the adsorption favoured in the acidic pH, where they observed an efficiency of 88.17% for 20 mg/L of Congo red solution with 6g/L dose of Graphene oxide impregnated chitosan–PVA hydrogel. The high surface area of the hydrogel, along with the oxygen and nitrogen groups present in the composite helped in the high adsorption efficiency of the dye[60]. Table 2 summarizes some of the available literature on the use of chitosan-GO composites for dye removal.

Table 2: Examples of chitosan-GO composites for dye removal.

Material	Concentration of adsorbent	Concentration of dye	Percentage adsorption	Reference
GO functionalized with vinyl triethoxy silane which was subsequently used as a chemical crosslinker to synthesize the NCH of CS and CMC (CS/CMC-NCH)	0.4 g/L	50 mg/L dye solution of MB dye	99 %	52
GO functionalized with vinyl triethoxy silane which was subsequently used as a chemical crosslinker to synthesize the NCH of CS and CMC (CS/CMC-NCH)	0.6 g/L	50 mg/L dye solution of MB dye	82%	52
CS-GO composite		Methylene blue	115 mg g−1	20
CS-GO membrane		MB	95 %	58
CS-GO membrane		M0	68-99 %	58
CS-Magnetic GO	5mg/ml	2-naphthol	99 %	59
Graphene oxide impregnated chitosan–PVA hydrogel	6g/L	Congo red	88.17%	60
Graphene oxide/chitosan aerogel microspheres		Methylene Blue	584.6 mg g-1	44

6. Chitosan-GO composites for the removal of pesticides

Another important category of water pollutants is pesticides. Pesticides such as polyphenols which are being widely used in the agricultural fields reaches out to different water streams and cause a major threat to the quality of water. Zhang et. al utilised CS-reduced graphene oxides composites with 3D structures to test the adsorption capacity for 70 pesticides including catechins (polyphenol compounds) and caffeine. They observed that the 3D structured composite of CS-reduced graphene oxide had a better adsorption capacity over pristine GO or pristine CS. The increased adsorption is attributed to the increased hydrophobic interaction between the reduced GO and catechin. Caffeine also showed a similar trend, with an increase in adsorption capacity when CS is grafted to rGO to form a 3D structure. In this case, the increase in adsorption is attributed to the increased electrostatic interaction between GO in the composite and caffeine. The results were far better when compared the adorption with the traditional adsorbents like primary-secondary amine (PSA), graphitized carbon black (GCB) and C18. The authors tested the prepared composites for seventy other pesticides and observed that sixty one out of them showed acceptable recovery[61]. Table 3 shows some of the pesticides being removed or reduced by the use of chitosan-GO composites.

Table 3: Examples of chitosan-GO composites for pesticide removal.

Adsorbent	Pesticide	Capacity	Reference
3D CS-rGO	Catechin	179.3 mg g -1	61
3D CS-rGO	Caffeine	63.6 mg g -1	61

7. Hydrogels and aerogels of Chitosan and GO for water treatment

Hydrogels are solid porous network structures, where the three-dimensional porosity is filled with solvents. In general, hydrogels possess high surface area and act as good adsorbent for the same reason. Chitosan hydrogels are not an exception to this effective adsorption capacity in addition to which it also possesses high reactivity due to the presence of reactive functional groups. However, these hydrogels suffer from inadequate thermal and mechanical stability to be employed for any practical applications. Cross-linking is an efficient way to increase these drawbacks, but at an expense of decreased adsorption efficiency.

Addition of nanofillers, especially two-dimensional materials with very high surface area, can simultaneously increase the thermal and mechanical stability along with the improvement in the adsorption of various pollutants prevalent in the water. For example, Chen et. al, synthesised a hydrogel of chitosan and graphene oxide by adding GO to the chitosan dissolved in dilute acetic acid which in turn results into the self-assembly of the GO sheets and the chitosan. Here, GO sheets formed the 3D network structure, where chitosan helped as a crosslinker by the effective reaction between the amino groups of the polymer with the hydroxyl groups of GO by forming stable hydrogen bonding. They have used a syringe filled with the composite hydrogels and it was observed to be an excellent adsorbent for various dyes falling into the category of anionic dyes, cationic dyes and even for heavy metals such as Cu(II) and Pb(II). The observed adsorption capacity was greater than 300 mg/L for both the cationic and anionic dyes with increase in adsorption with increase in GO content[62].

P Yu et.al, prepared a self-assembled hydrogel of montmorillonite- graphene oxide- chitosan hydrogel for the effective removal of highly toxic Cr (VI). Montmorillonite is also having a sheet like structure similar to GO, with a high surface area at the same time an economically more feasible option because of its natural occurrence. FTIR and WAXD showed the formation of chemical bonding between CS and GO and also confirmed the in-situ reduction of GO to reduced graphene oxide. The hydrogen bonding of CS with GO and the intercalation of MT resulted in a highly porous sponge like structure as shown in the Fig. 7. The sorption capacity for Cr (VI) was found to be 87.03 mg/g at 288 K and followed a Langmuir adsorption isotherm[63].

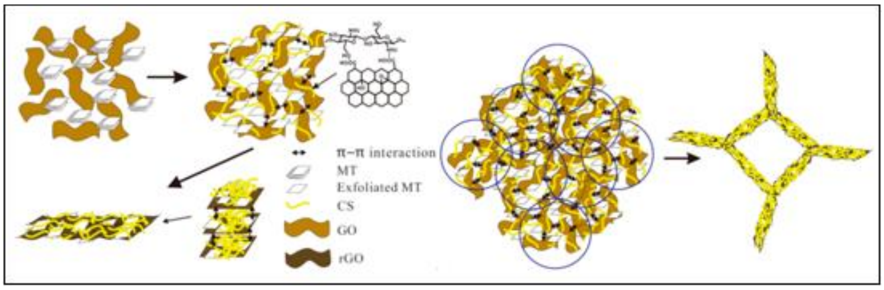

Figure 7: The pore formation in polymer composites. Reprinted with permission from {ACS Sustainable Chem. Eng. 2017, 5, 2, 1557–1566}. Copyright {2016} American Chemical Society. [63]

Selenium, one of the less studied carcinogenic materials which can also cause other potential hazards such as reproductive irregularities, juvenile mortalities etc, mainly reaching the soil and water samples not only from the natural sources but also from the petroleum and metal refineries is also found to be effectively removed by chitosan-based hydrogels. Bandara et. al synthesised a composite crosslinked hydrogel of chitosan-polyethyleneimine-graphene oxide and studied the selenium adsorption from water samples at various pH. It was observed that the effective removal is possible in acidic medium, with the maximum adsorption capacity of 1.62 mg/g[64]

The aerogels of CS and its composites, formed by the removal of the solvent from the hydrogels, without causing the breakdown or shrinkage of the initial structure is an even better adsorbent due to its extensive porosity (mostly greater than 90 %).For example, an aerogel of CS-GO composites formed by the freeze drying of its precursor hydrogel showed an adsorption capacity of 686.89 mg/g for methyl orange and 573.47 mg/g for amido black. SEM images obtained (Fig. 8) showed the sheet like GO arranged in an ordered porous form, with porosity more than 97 %[63]. Table 4 shows few examples of the use of composite aerogels of chitosan-GO for dye removal.

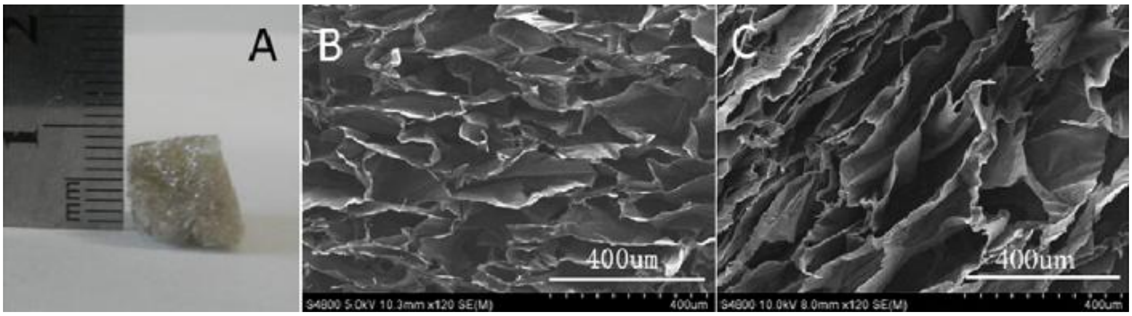

Figure 8: SEM images chitosan composites with rGO[63].Reprinted with permission from {ACS Sustainable Chem. Eng. 2017, 5, 2, 1557–1566}. Copyright {2016} American Chemical Society

Table 4: Examples of chitosan-GO aerogels for dye removal.

Adsorbent Material	Dye Adsorption capacity	Metal adsorption capacity	Reference
CS-GO Hydrogel	MB > 300 mg/L Eosin Y > 300 mg/L	Cu (II) – 70 mg/l Pb (II) – 90 mg/L	62
Chitosan/reduced graphene oxide/montmorillonite composite Hydrogel	-	Cr (VI) - 87.03 mg/g	63
CS-PEI-GO Hydrogel		Se – 1.62 mg/g	64
CS- GO Aerogel	MO -686.89 mg/g Amido black 10 B - 573.47 mg/g		65

8. Summary and Future Perspectives

The review summarizes some of the important findings in the field of chitosan-GO and its derivatives composites for the water purification applications. It is clear that, these 2D-nanofiller incorporated natural polymer composites are one among the most suitable materials for the water treatment processes. However more research could be conducted on the synthesis and applications of mechanically and thermally stable composite aerogels of chitosan for the efficient removal of various water pollutants.

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